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What we claim is:

- A method of treating a metal substrate, comprising:
 - (a) providing a metal substrate; and
 - (b) applying a coating of a silane composition onto the metal substrate, said silane composition comprising at least one substantially unhydrolyzed aminosilane which has one or more secondary or tertiary amino groups.
- 2. The method of claim 1, wherein said aminosilane comprises:

$$\begin{bmatrix} R'O - S_i - R^2 \\ OR' \end{bmatrix}_N X - \begin{bmatrix} R^5 \\ QR' \end{bmatrix}_{y}$$

wherein:

10 -n is either 1 or 2;

-y = (2-n);

-each R^1 is individually chosen from the group consisting of: C_1 - C_{24} alkyl and C_2 - C_{24} acyl;

-each R² is individually chosen from the group consisting of: substituted aliphatic groups, unsubstituted aliphatic groups, substituted aromatic groups, and unsubstituted aromatic groups;

-R⁵ is chosen from the group consisting of: hydrogen, C_1 - C_{10} alkylene, C_1 - C_{10} alkylene substituted with one or more amino groups, C_1 - C_{10} alkenylene, C_1 - C_{10} alkenylene substituted with one or more amino groups, arylene, and alkylarylene;

-X is either:

-wherein each R³ is individually chosen from the group consisting of: hydrogen, substituted and unsubstituted aliphatic groups, and substituted and unsubstituted aromatic groups; and

- -R⁴ is chosen from the group consisting of: substituted and unsubstituted aliphatic groups, and substituted and unsubstituted aromatic groups; and wherein, when n=1, at least one of said R³ and said R⁵ is not hydrogen.
- 3. The method of claim 1, wherein said aminosilane comprises a bis-silyl aminosilane having two trisubstituted silyl groups, wherein the substituents are individually chosen from the group consisting of alkoxy, aryloxy and acyloxy.
- 10 4. The method of claim 3, wherein said bis-silyl aminosilane comprises:

wherein:

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-each R^1 is individually chosen from the group consisting of: C_1 - C_{24} alkyl and C_2 - C_{24} acyl;

-each R² is individually chosen from the group consisting of: substituted aliphatic groups, unsubstituted aliphatic groups, substituted aromatic groups, and unsubstituted aromatic groups; and

-X is either:

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- -wherein each R³ is individually chosen from the group consisting of: hydrogen, substituted and unsubstituted aliphatic groups, and substituted and unsubstituted aromatic groups; and
- -R⁴ is chosen from the group consisting of: substituted and unsubstituted aliphatic groups, and substituted and unsubstituted aromatic groups.

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- 5. The method of claim 4, wherein each R¹ is individually chosen from the group consisting of: ethyl, methyl, propyl, iso-propyl, butyl, iso-butyl, sec-butyl, ter-butyl and acetyl.
- 6. The method of claim 4, wherein X is chosen from the group consisting of:
 a C-Si bond, C₁ C₆ alkylene, C₁ C₆ alkenylene, C₁ C₆ alkylene substituted with at least one amino group, C₁ C₆ alkenylene substituted with at least one amino group, arylene, and alkylarylene.
 - 7. The method of claim 4, wherein each R² is individually chosen from the group consisting of: hydrogen, ethyl, methyl, propyl, iso-propyl, butyl, iso-butyl, sec-butyl, ter-butyl and acetyl.
 - 8. The method of claim 1, wherein said aminosilane is chosen from the group consisting of: bis-(trimethoxysilylpropyl)amine, bis-(triethoxysilylpropyl)amine, bis-(triethoxysilylpropyl)ethylene diamine, N-[2-(vinylbenzylamino)ethyl]-3-aminopropyltrimethoxy, and aminoethyl-aminopropyltrimethoxy silane.
 - 9. The method of claim 1, wherein said silane composition further comprises at least one additional substantially unhydrolyzed silane.
 - 10. The method of claim 3, wherein said silane composition further comprises at least one substantially unhydrolyzed bis-silyl polysulfur silane.

11. The method of claim 10, wherein said bis-silyl polysulfur silane comprises:

wherein each R^1 is an alkyl or an acetyl group, and Z is $-Q-S_X-Q-$, wherein each Q is an aliphatic or aromatic group, and x is an integer of from 2 to 10.

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- 12. The method of claim 11, wherein each R¹ is individually chosen from the group consisting of: ethyl, methyl, propyl, iso-propyl, butyl, iso-butyl, sec-butyl, ter-butyl and acetyl.
- 13. The method of claim 11, wherein each Q is individually chosen from the group consisting of: C_1 C_6 alkyl (linear or branched), C_1 C_6 alkyl substituted with one or more amino groups, C_1 C_6 alkeryl substituted with one or more amino groups, benzyl, and benzyl substituted with C_1 C_6 alkyl.
- 14. The method of claim 10, wherein said at least one bis-silyl polysulfur silane comprises a bis-(triethoxysilylpropyl) sulfide having 2 to 10 sulfur atoms.
- 15. The method of claim 10, wherein said at least one bis-silyl polysulfur silane comprises bis-(triethoxysilylpropyl) tetrasulfide.
- 16. The method of claim 10, wherein the ratio of bis-silyl aminosilanes to bis-silyl polysulfur silanes in said silane composition is between about 1:10 and about 10:1.

- 17. The method of claim 10, wherein the ratio of bis-silyl aminosilanes to bis-silyl polysulfur silanes in said silane composition is between about 1:3 and about 1:1.
- 18. The method of claim 10, wherein said silane composition further comprises a non-aqueous solvent.
- 19. The method of claim 18, wherein said solvent is chosen from the group consisting of: ethanol, methanol, propanol and isopropanol.
- 20. The method of claim 1, wherein said silane composition consists essentially of at least one substantially unhydrolyzed bis-silyl aminosilane and at least one substantially unhydrolyzed bis-silyl polysulfur silane.
- 21. The method of claim 20, wherein said silane composition consists essentially of said at least one substantially unhydrolyzed bis-silyl aminosilane, said at least one substantially unhydrolyzed bis-silyl polysulfur silane, and a non-aqueous solvent.
- 22. The method of claim 10, further comprising the step of drying said coating.
- 23. The method of claim 1, further comprising the step of adhering a polymer layer to said coating.
- 24. The method of claim 23, wherein said polymer layer comprises rubber.
- 25. The method of claim 24, wherein said polymer layer comprises a sulfurcured rubber.

- 26. The method of claim 10, further comprising the step of adhering a polymer layer to said coating.
- 27. The method of claim 26, wherein said polymer layer comprises rubber.
- 28. The method of claim 27, wherein said polymer layer comprises a sulfurcured rubber.
- 29. A method of adhering rubber to a metal substrate, comprising:
 - (a) applying a coating of a silane composition onto a metal substrate, said silane composition comprising:
 - -a bis-silyl aminosilane, or the hydrolysate or partial hydrolysate thereof; and
 - -a bis-silyl polysulfur silane, or the hydrolysate or partial hydrolysate thereof; and
 - (b) adhering rubber to said coating.
- 30. The method of claim 29, wherein said bis-silyl aminosilane comprises an aminosilane having two trisubstituted silyl groups, wherein the substituents are individually chosen from the group consisting of alkoxy, aryloxy and acyloxy.
- 31. The method of claim 30, wherein said bis-silyl aminosilane comprises:

wherein:

-each R^1 is individually chosen from the group consisting of: $C_1 - C_{24}$ alkyl and $C_2 - C_{24}$ acyl;

-each R² is individually chosen from the group consisting of: substituted aliphatic groups, unsubstituted aliphatic groups, substituted aromatic groups, and unsubstituted aromatic groups; and

-X is either:

-wherein each R³ is individually chosen from the group consisting of: hydrogen, substituted and unsubstituted aliphatic groups, and substituted and unsubstituted aromatic groups; and

-R⁴ is chosen from the group consisting of: substituted and unsubstituted aliphatic groups, and substituted and unsubstituted aromatic groups.

- 32. The method of claim 31, wherein each R¹ is individually chosen from the group consisting of: ethyl, methyl, propyl, iso-propyl, butyl, iso-butyl, sec-butyl, ter-butyl and acetyl.
- 33. The method of claim 31, wherein X is chosen from the group consisting of: a C-Si bond, $C_1 C_6$ alkylene, $C_1 C_6$ alkenylene, $C_1 C_6$ alkylene substituted with at least one amino group, $C_1 C_6$ alkenylene substituted with at least one amino group, arylene, and alkylarylene.
- 34. The method of claim 31, wherein each R² is individually chosen from the group consisting of: hydrogen, ethyl, methyl, propyl, iso-propyl, butyl, iso-butyl, sec-butyl, ter-butyl and acetyl.
- 35. The method of claim 29, wherein said bis-silyl aminosilane is chosen from the group consisting of: bis-(trimethoxysilylpropyl)amine, bis-(triethoxysilylpropyl)amine, and bis-(triethoxysilylpropyl)ethylene diamine.

36. The method of claim 29, wherein said bis-silyl polysulfur silane comprises:

wherein each R^1 is an alkyl or an acetyl group, and Z is $Q-S_X-Q$, wherein each Q is an aliphatic or aromatic group, and X is an integer of from 2 to 10.

- 37. The method of claim 36, wherein each R¹ is individually chosen from the group consisting of: ethyl, methyl, propyl, iso-propyl, butyl, iso-butyl, sec-butyl, ter-butyl and acetyl.
- 38. The method of claim 36, wherein each Q is individually chosen from the group consisting of: $C_1 C_6$ alkyl (linear or branched), $C_1 C_6$ alkenyl (linear or branched), $C_1 C_6$ alkyl substituted with one or more amino groups, $C_1 C_6$ alkenyl substituted with one or more amino groups, benzyl, and benzyl substituted with $C_1 C_6$ alkyl.
- 39. The method of claim 29, wherein said at least one bis-silyl polysulfur silane comprises a bis-(triethoxysilylpropyl) sulfide having 2 to 10 sulfur atoms.
- 40. The method of claim 39, wherein said at least one bis-silyl polysulfur silane comprises bis-(triethoxysilylpropyl) tetrasulfide.
- 41. The method of claim 29, wherein said metal substrate is chosen from the group consisting of:
 - -zinc and zinc alloys;

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-métal substrates having a zinc-containing coating;

- -steel;
- -aluminum and aluminum alloys;
- -copper and copper alloys;
- -tin and tin alloys; and
- -metal substrates having tin-containing coatings
- 42. The method of claim 29, wherein the silanes in said silane composition are substantially unhydrolyzed.
- 43. The method of claim 42, wherein the ratio of bis-silyl aminosilanes to bis-silyl polysulfur silanes in said silane composition is between about 1:10 and about 10:1.
- 44. The method of claim 42, wherein said silane composition further comprises a non-aqueous solvent.
- 45. The method of claim 29, wherein said silane composition consists essentially of said at least one substantially unhydrolyzed bis-silyl aminosilane and said at least one substantially unhydrolyzed bis-silyl polysulfur silane.
- 46. The method of claim 29, wherein the silanes in said silane composition are at least partially hydrolyzed.
- 47. The method of claim 46, wherein the ratio of bis-silyl aminosilanes to bis-silyl polysulfur silanes in said silane composition is between about 1:10 and about 10:1.
- 48. The method of claim 47, wherein said silane composition further comprises water and a solvent.

- The method of claim 48, wherein the ratio of water to solvent in said silane composition is between about 1:1 and about 1:20.
- 50. The method of claim 46, wherein the pH of said silane composition is between about 4 and about 7.
- 51. The method of claim 29, wherein said rubber comprises a sulfur-cured rubber.
- 52. The method of claim 51, wherein said step of adhering said sulfur-cured rubber comprises applying an uncured rubber compound directly onto said silane coating, and thereafter curing said rubber compound.
- 53. The method of claim 52, further comprising the step of drying said silane coating prior to applying said uncured rubber compound.
- 54. A silane composition comprising:
 - -at least one substantially unhydrolyzed aminosilane which has one or more secondary or tertiary amino groups; and
 - -at least one other substantially unhydrolyzed silane
- 55. The silane composition of claim 54, wherein said aminosilane comprises:

$$\begin{bmatrix} R'O - S; - R^2 \\ OR' \end{bmatrix}_{N} \times \begin{bmatrix} R^5 \\ N \end{bmatrix}_{y}$$

wherein:

-n is either 1 or 2;

-y = (2-n);

-each R^1 is individually chosen from the group consisting of: C_1 - C_{24} alkyl and C_2 - C_{24} acyl;

-each R² is individually chosen from the group consisting of: substituted aliphatic groups, unsubstituted aliphatic groups, substituted aromatic groups, and unsubstituted aromatic groups;

-R⁵ is chosen from the group consisting of: hydrogen, C_1 - C_{10} alkylene, C_1 - C_{10} alkylene substituted with one or more amino groups, C_1 - C_{10} alkenylene, C_1 - C_{10} alkenylene substituted with one or more amino groups, arylene, and alkylarylene;

-X is either:

$$R^3$$
 R^3 R^3 R^3 R^4 or R^4

-wherein each R³ is individually chosen from the group consisting of: hydrogen, substituted and unsubstituted aliphatic groups, and substituted and unsubstituted aromatic groups; and

-R⁴ is chosen from the group consisting of: substituted and unsubstituted aliphatic groups, and substituted and unsubstituted aromatic groups; and wherein, when n=1, at least one of said R³ and said R⁵ is not hydrogen.

56. The silane composition of claim 54, wherein said aminosilane comprises:

$$R^{1}O - Si - R^{2} - X - R^{2} - Si - OR^{1}$$
 OR^{1}
 OR^{1}
 OR^{1}
 OR^{1}

wherein:

-each R^1 is individually chosen from the group consisting of: C_1 - C_{24} alkyl and C_2 - C_{24} acyl;

-each R² is individually chosen from the group consisting of: substituted aliphatic groups, unsubstituted aliphatic groups, substituted aromatic groups, and unsubstituted aromatic groups; and

-X is either:

-wherein each R³ is individually chosen from the group consisting of: hydrogen, substituted and unsubstituted aliphatic groups, and substituted and unsubstituted aromatic groups; and

-R⁴ is chosen from the group consisting of: substituted and unsubstituted aliphatic groups, and substituted and unsubstituted aromatic groups.

- 57. The silane composition of claim 54, wherein said aminosilane is chosen from the group consisting of: bis-(trimethoxysilylpropyl)amine, bis-(triethoxysilylpropyl)amine, and bis-(triethoxysilylpropyl)ethylene diamine.
- 58. The silane composition of claim 54, wherein said other substantially unhydrolyzed silane comprises an organofunctional silane.
- 59. The silane composition of claim 56, wherein said other substantially unhydrolyzed silane comprises a bis-silyl polysulfur silane.
- 60. The silane composition of claim 59, wherein said bis-silyl polysulfur silane comprises:

wherein each R^1 is an alkyl or an acetyl group, and Z is $-Q-S_x-Q-$, wherein each Q is an aliphatic or aromatic group, and x is an integer of from 2 to 10.

- 61. The silane composition of claim 59, wherein said at least one bis-silyl polysulfur silane comprises a bis-(triethoxysilylpropyl) sulfide having 2 to 10 sulfur atoms.
- 62. The silane composition of claim 59, wherein the ratio of bis-silyl aminosilanes to bis-silyl polysulfur silanes in said silane composition is between about 1:10 and about 10:1.
- 63. The silane composition of claim 59, wherein said silane composition further comprises a non-aqueous solvent.
- 64. The silane composition of claim 59, wherein said silane composition consists essentially of said at least one substantially unhydrolyzed bis-silyl aminosilane and said at least one substantially unhydrolyzed bis-silyl polysulfur silane.
- 65. A silane coated metal substrate made in accordance with the method of claim 1.

☼. A metal substrate having a polymer layer thereon, made in accordance with the method of claim 23.

A metal substrate having rubber adhered thereto made in accordance with the method of claim 29.

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